Supporting Information

Facile noninjection synthesis and photocatalytic properties of wurtzite-phase CuGaS₂ nanocrystals with elongated morphologies

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Experimental Details

Materials. 1-Dodecanethiol (DDT, >98%), oleic acid (OA, 90%), trioctylamine (TOA, \geq 98%), oleylamine (OM, 70%) and Rhodamine B (RhB) were purchased from Aldrich and used without further purification. The diethyldithiocarbamate complexes, Cu(S₂CNEt₂)₂ and Ga(S₂CNEt₂)₃, were synthesized based on previously published procedures.¹

Synthesis of wurtzite-phase CuGaS₂ nanocrystals with elongated shapes. In a typical synthesis, DDT (5 mL) and OA (5 mL) were added to a 50-mL three-neck flask containing 0.1 mmol each of the metal dithiocarbamate precursors (i.e., Cu(S₂CNEt₂)₂ and Ga(S₂CNEt₂)₃). The mixture was degassed at 100 °C for 20 min prior to heating under Ar to 280 °C. The resulting mixture was kept at 280 °C for 30 min before cooling to 40 °C with the aid of a H₂O bath. Ethanol was added to precipitate the nanocrystals, and this was followed by centrifugation. The yellow-orange solid obtained was washed thoroughly with hexane and ethanol. The assynthesized nanocrystals exhibit tadpole-like morphology. Replacing OA with TOA yielded rod-shaped nanocrystals.

Phase-selective synthesis of CuGaS₂ nanocrystals. Phase-control was achieved by varying the coordinating solvent/capping ligand used in the synthetic procedure described above. The wurtzite phase was obtained with the use of the following solvent pairs: (1) DDT and OA, (2) DDT and TOA, and (3) DDT and OM. Meanwhile, tetragonal chalcopyrite or cubic zinc-blende phase was produced when the solvent mixtures used are: (1) OM and TOA and (2) OM and OA.

Characterization. Transmission electron microscopy (TEM) images were primarily taken using a Philips EM300 electron microscope operated at an accelerating voltage of 300 kV. Additional imaging was performed using a JEOL 2100 electron microscope (accelerating voltage: 200 kV), which is equipped with an energy-dispersive X-ray (EDX) detector that was used for elemental analysis. In preparing the specimens, a drop of nanocrystals dispersed in hexane was placed on the surface of a lacey formvar/carbon 300-mesh Cu grid or onto formvar/carbon 200-mesh Ni grid. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Fisher Scientific Thetaprobe XPS spectrometer with an Al K α monochromatic X-ray source at 15 kV and 100 W. X-ray diffraction (XRD) patterns were collected on a Bruker GADDS D8 Discover diffractometer using Cu K α radiation (1.5418 Å). Room-temperature absorption spectra were recorded using a Shimadzu UV-3150 UV-Vis-NIR spectrophotometer. The nanocrystal samples were dispersed in CHCl₃ and loaded into a quartz cuvette. **Photocatalytic Evaluation.** The photocatalytic activity of the elongated CGS nanocrystals was evaluated for RhB degradation under visible light illumination. The CGS nanocrystal sample (7 mg) was first suspended in 20 mL of deionized H₂O in a glass vial. An aqueous solution of RhB (200 μ L, 1 mM) was then added to the suspension. Prior to irradiation, the resulting mixture was continuously stirred in the dark for 3.5 h to ensure the establishment of an adsorption-desorption equilibrium. The suspension was illuminated with visible light using a 500-W Philips QVF135 Halolite lamp and a cutoff filter at a 15-cm distance. The cut-off filter was used to completely eliminate any radiation at wavelength below 430 nm. At a specified time interval, 1.5 mL of the irradiated suspension were taken out and centrifuged to remove the solid nanocrystal catalyst. The RhB dye concentration in the filtrate was monitored by measuring the absorbance of RhB at 553 nm. A decrease in intensity of the RhB absorption peak is indicative of the decrease in RhB concentration due to degradation. The degradation efficiency (*E*_{ff}) was determined using the equation, *E*_{ff} (%) = (1 - C/C_0) × 100%, where C₀ and C are the absorbance of the dye solution at 553 nm before and after irradiation, respectively. For comparison purposes, a similar experiment was performed in the dark.

Supporting Figures



Fig. S1. High-resolution XPS analysis of elongated CGS nanocrystals showing the Cu 2p (red), Ga 2p (green) and S 2p (blue) spectra.



Fig. S2. Rietveld refinement of the XRD patterns obtained for CGS nanocrystals with (a) tadpole-shaped and (b) rod-shaped morphologies. Displayed are the observed (blue) and refined (red) patterns, the difference curve (grey), and the reflection positions of wurtzite-phase CGS (blue sticks at the bottom). The refined lattice parameters (*a* and *c*), R_{wp} and R_p are listed below.

wurtzite CGS	a (Å)	c (Å)	$R_{ m wp}$	R _p
(a) tadpole-shaped	3.7531	6.1813	0.0621	0.0485
	error = 0.0154	error = 0.0253		
(b) rod-shaped	3.7385	6.1720	0.0938	0.0715
	error = 0.0301	error = 0.0496		



Fig. S3. (a-b) TEM images and (c) XRD pattern of snake-shaped wurtzite-phase CGS nanocrystals synthesized using a solvent mixture of DDT and OM. The high-resolution TEM image of the boxed area in (b) is shown on the right. The red stick pattern shown in (c) is the simulated pattern for $CuGaS_2$ having the hexagonal wurtzite structure.



Fig. S4. XRD pattern of CGS nanocrystals synthesized using a solvent mixture of (a) OM and TOA and (b) OM and OA. The peaks marked with an asterisk (*) are minor impurity peaks. The corresponding TEM images are shown as insets. The red stick pattern shown is from standard JCPDS file for tetragonal CGS (75-0103) whereas the blue stick pattern is the simulated pattern for CGS having the cubic zinc-blende structure. Because of the similar diffraction patterns of the tetragonal and cubic CGS, and the broadening of the experimental diffraction peaks due to the small crystallite size, it is difficult to distinguish between the two phases based on powder XRD data.



Fig. S5. Temporal evolution of the absorption spectra of the aqueous RhB solution in the presence of CGS nanocrystals in the dark.

Exciton Bohr radius of bulk CGS:

The exciton Bohr radius $(a_{\rm B})$ is calculated using the equation:

$$a_{\rm B} = a_{\rm o} \varepsilon m_{\rm o} \left(\frac{1}{m_{\rm e}^*} + \frac{1}{m_{\rm h}^*} \right)$$

where a_0 is the hydrogen atom Bohr radius = 0.0529 nm; ε is the dielectric constant; m_0 is the free electron mass; and m_e^* and m_h^* are the effective mass of electron and hole, respectively. The reported values^{2,3} for CGS are $\varepsilon = 8.5$, $m_e^* = 0.13m_0$ and $m_h^* = 0.69m_0$. Using these values and the equation above, a_B for CGS is estimated to be 4.1 nm.

References:

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